J. Andrasko,[1] *Ph.D. and S. Ståhling*[2]

Time Since Discharge of Pistols and Revolvers

ABSTRACT: The estimation of time since the latest discharge of pistols and revolvers has been achieved by the Solid Phase Microextraction (SPME) sampling technique and the GC/TEA analytical system. The TEA2 compound, which in our previous work (1) was observed in barrels of shotguns and rifles as well as inside spent cartridges, was also detected in pistols and revolvers. The amount of this compound was very low in short-barreled small arms and its escape from the barrel could generally be measured for only a few days or up to two weeks after the latest discharge. To improve the detection of TEA2 compound, the SPME sampling time was prolonged and fibers coated by Carboxen/polydimethylsiloxane were used.

The decrease of the TEA2 peak with time after shooting from pistols is nonexponential but the curve-fitting procedure proposed for the estimation of time since discharge of shotguns and rifles is difficult to apply as the decay is very rapid. Therefore, the detection of TEA2 compounds in small arms should be interpreted that the firearm had been used very recently. The amount of volatile decomposition products of smokeless powder increased significantly with the length of the barrel when firearms of the same caliber, but with different barrel lengths were investigated.

KEYWORDS: forensic science, firearms, time since discharge, SPME, GC, GC-TEA, firearm discharge residues, pistols, revolvers

The Solid Phase Microextraction (SPME) technique has been successfully used for the detection of various volatile compounds inside firearm barrels, as well as inside spent cartridges, for the estimation of the time since the latest discharge of the firearms and cartridges (1–4). One of the compounds formed on shooting, whose escape from the barrel or shell is generally suitable for monitoring time since the latest discharge, has been designated as the TEA2 compound. This compound is detected with high sensitivity using the TEA (thermal energy analyzer) detector in the GC-TEA system. Shotguns and rifles are equipped with long barrels. In firearms with long barrels the concentration of the volatile decomposition products of smokeless powder is generally high and the TEA2 peak may be detected for months after the latest discharge. Pistols and revolvers have relatively short barrels (the ratio between the length of the barrel and caliber is low) and the amount of TEA2 compound deposited inside their barrels is very low.

In this study, a slightly modified SPME technique was applied for the detection of the escape of the TEA2 compound from pistol and revolver barrels. An attempt to prevent the TEA2 compound from escaping the barrel by freezing the firearm was found successful. To stop or slow down this escaping/degradation process is necessary when the suspect firearm is available, but the analysis using the GC-TEA system cannot be carried out immediately. Most of the experiments were carried out with pistols (semiautomatic), but the results for revolvers seemed to be very similar.

Materials and Methods

Solid-Phase Microextraction

Fused silica fibers with an 85 μm Carboxen/polydimethylsiloxane coating were purchased from Supelco (Bellefonte, PA) and used in most of the experiments. Fibers coated by polyacrylate (used in our previous studies) and Carbowax/divinylbenzene have been compared in some experiments. New fibers were conditioned at 270°C for 2–3 h by heating in a GC injector. Prior to sampling the fiber was conditioned for 10 min at 170°C and then allowed to cool down at room temperature for an additional 10 min. Blank analyses were performed to make sure that the fiber and the chromatographic system were clean and free from interfering substances.

Sampling from Pistols and Revolvers

The firearm was placed horizontally. To ensure that the sampling geometry was as constant as possible, a small cork was put in the muzzle. The SPME sampling was performed by pushing the needle of the SPME holder through a small aperture in the middle of the cork inside the barrel as far as possible. The fiber position inside the same type of firearm was kept constant. The coated fiber on the top of the SPME needle was exposed to the atmosphere inside the barrel for 40 min. The samplings were performed at room temperature (22–23°C). Figure 1 illustrates the SPME sampling from pistols.

Gas Chromatographic Analyses

The GC-TEA system was used for quantitative analysis of compounds adsorbed by headspace SPME from inside pistol/revolver barrels. This system was described in the previous study (1) and the temperature program modified later (3). The thermal desorption of the SPME fiber was performed at 170°C in splitless mode of injection. The liner used was purchased from Supelco (SPME Injection Sleeve for Hewlett Packard), especially designed for desorption of volatile compounds from SPME fibers. The inner diameter is only 0.75 mm, which means that the desorption volume inside the liner is very small. The peak broadening of the most volatile compounds is thus minimized. The liner was used empty.

[1] Associate Professor, SKL, National Laboratory of Forensic Science, S-58194 Linkoping, Sweden.
[2] Firearm Investigator, SKL, National Laboratory of Forensic Science, S-58194 Linkoping, Sweden.

FIG. 1—*Sampling from pistol barrels. The SPME fiber is exposed to the atmosphere inside the barrel for 40 min at room temperature. The pistol shown is a Walther of 7.65 mm caliber. Note the use of a cork in the pistol muzzle. The needle of the SPME device is pushed inside the barrel through the small aperture in the middle of the cork. The sampling position and geometry is thus kept constant.*

Results and Discussion

Decomposition Products of Smokeless Powder Detected Inside Pistol/Revolver Barrels

Similar to our results with rifles, the only compound detected in pistol and revolver barrels after shooting, escaping from the barrel with time after shooting, and suitable for estimation of time since the latest discharge of the firearm was the TEA2 compound. In comparison with shotguns, the TEA2 peak detected in pistols/revolvers was very much weaker, approximately three orders of magnitude weaker (Fig. 2). The amount of TEA2 detected one day after the shooting is generally weaker than that detected inside rifle barrels and comparable with the amount detected inside spent cartridges. To improve the detection of the volatile TEA2 compound, the sampling time was increased to 40 min and a new type of SPME fiber consisting of a 85 μm Carboxen/polydimethylsiloxane adsorption layer was used for sampling from pistols and revolvers. This type of fiber adsorbed a higher amount of TEA2 compound in the same sampling time in comparison with a polyacrylate fiber used in our previous work. Also, Carboxen/divinylbenzene fiber was found less effective for this purpose. The GC-TEA system is sensitive for detection of nitro- and nitroso compounds. However, it is not a system that identifies the detected compounds. We are not sure that the TEA2 peak observed in shotguns, pistols or rifles represents the same compound. It can be seen in Fig. 2 that the retention time of this peak detected in pistols is longer than that observed in shotguns. The increase in retention time with decreasing concentration of TEA2 compound depends on rather bad chromatographic behavior of this unstable compound (see, e.g., Fig. 5 in Ref 3). It is also possible that the very strong peak detected in shotguns may represent a mixture of two or several compounds formed on the decomposition of the propellant. The designation TEA2 is due only to this peak position in the chromatogram, where the first peak represents compounds not retained by the chromatographic system used. The common feature is that the concentration of these compounds decreases rapidly with time after the shooting. No volatile TEA peaks are detected in barrels of firearms that have not been used for a long time.

So far, we have not succeeded in identifying the chemical nature of TEA2 compound/compounds. The mass spectrum of the com-
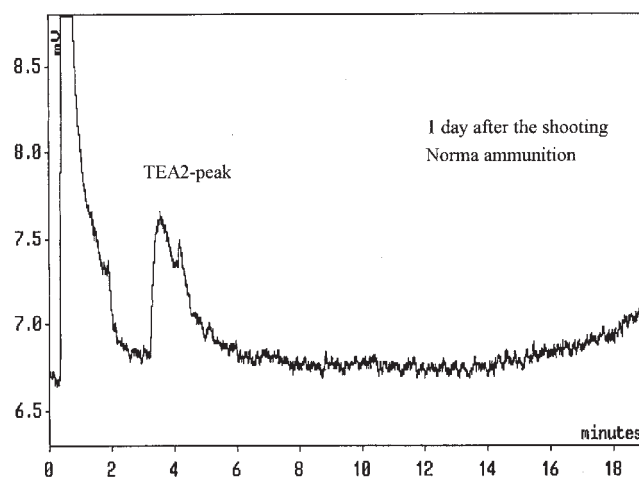
Shotgun (12/70)
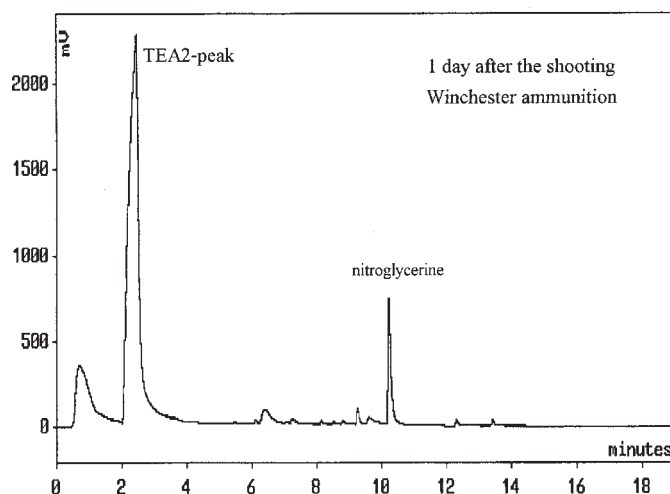
7.65 mm Walther pistol

FIG. 2—*Comparison of the amount of TEA2 compound detected one day after shooting (a single shot) inside a 7.65 mm Walther pistol and a double-barreled shotgun (12/70), respectively. Note the enormous difference in this concentration—it is about three orders of magnitude weaker in the pistol.*

pound observed in shotguns has been obtained, but this spectrum did not match with any known spectrum in our library of mass spectra. The compound with the same mass spectrum was also detected in pistols a short time after shooting, but the sensitivity of the GC/MS system was not sufficient to detect the compound one day or later after shooting.

The amount of TEA2 compound detected in pistol barrels decreased with time after discharge in a manner similar to that observed for other types of firearms and spent cartridges. This decay is very rapid during the first days after the shooting. The decay of the TEA2 peak detected in Walther pistols, caliber 7.65 and 9 mm, is shown in Fig. 3. As the amount of TEA2 compound observed is very low, the decay can be followed only for a few days after the discharge. The detection limit (defined as three times the standard deviation of the peak-to-peak noise) for this peak in our GC/TEA system was estimated to about 0.1 mV (peak height). Similar to its decay in shotguns and rifles, the decay of the TEA2 peak with time since discharge was nonexponential in pistols and revolvers. Figure 4 shows this decay measured for Walther pistols, caliber 7.65 (model PP) and 9 mm (model P38). Winchester ammunition was used for these shootings, as that ammunition generally deposits more decomposition products on shooting. The decay of the TEA2 peak may, therefore, be measured with better precision and for a longer period after shooting. The y-axis is logarithmic, which
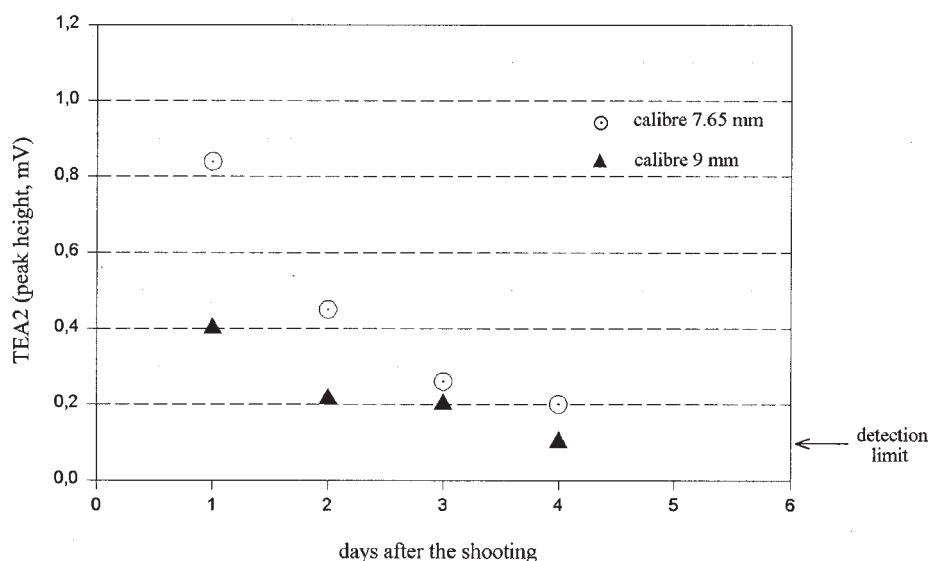
FIG. 3—*Decay of the TEA2 peak with time after firing one shot from Walther pistol with Norma ammunition (Carboxen/PDMS fiber, 40 min sampling). The results for pistols of two different calibers are shown. Due to the low amount of volatile decomposition products of the propellant inside pistol barrels, the decay of TEA2 compound can be followed for only a few days after the latest discharge. The detection limit for the TEA2 peak in our GC/TEA system has been estimated to be 0.1 mV.*
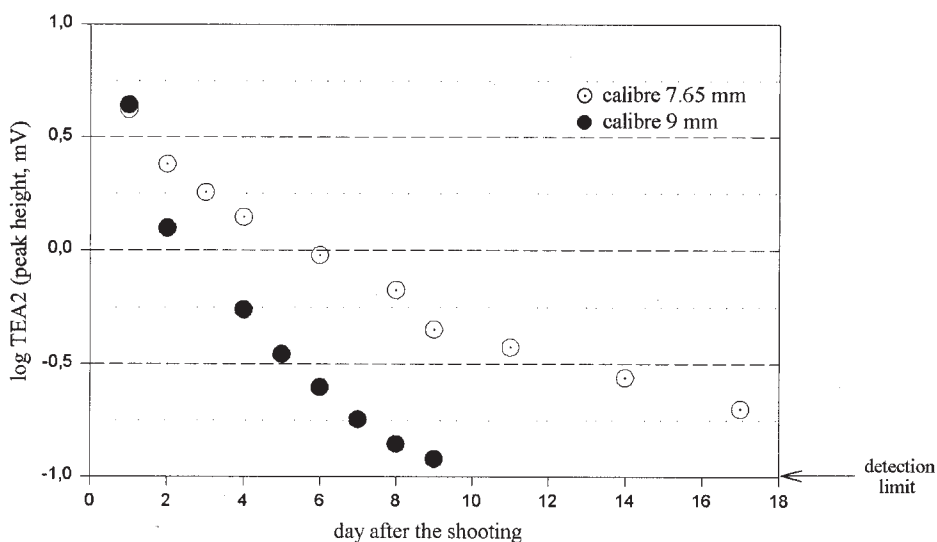
FIG. 4—*Escape of TEA2-compound from barrels of Walther pistols, calibers 7.65 and 9 mm, after firing one shot with Winchester ammunition. The pistols were stored at room temperature. Note that the y-axis uses a logarithmic scale and the decays are thus nonexponential. The detection limit for the TEA2 peak in our system was estimated to 0.1 mV, which corresponds to the value of −1.0 on the logarithmic scale. Winchester ammunition is generally one brand of ammunition that deposits the highest concentration of decomposition products inside firearm barrels upon shooting. The decay of the TEA2 compound may in this case be measured for about two weeks.*

TABLE 1—*Height of TEA2 peak detected on SPME sampling from Walther pistols, calibers 7.65 and 9 mm, one day after shooting with ammunition from various manufacturers. The sampling time was 40 min. The peak height values are in millivolts.*

Manufacturer Ammunition	Walther Pistol	
	Caliber 7.65 mm Model PP (9.8 cm Barrel)	Caliber 9 mm Model P38 (12.4 cm Barrel)
Norma	0.84[*]	0.40[*]
Winchester	4.2	4.4
Lapua	0.7	4.2
Fiocchi	0.5	2.6
Remington	0.55	1.8
Federal	4.8	8.6
Sellier & Bellot	0.9	
CCI Blazer, lead-free	3.3	ND
HP	0.35	1.3
Norma safety		4.4[**]
	Smith & Wesson revolver, caliber .357 length of barrel: 6 in.	
Winchester	6.0	
Norma	3.6	
Remington	2.5	

[*]The sampling time was only 30 min in this experiment.
[**]Sig Sauer pistol (caliber 9 mm) was used.
ND—not detectable

clearly shows that the decay is nonexponential. This nonexponentiality may be the result of different decay rates of the TEA2 compound from soot particles of different sizes or of the presence of two or more compounds contributing to the TEA2 peak. It seems that the rate of escape of the TEA2 compound is faster for pistols of larger caliber.

Pistols of both calibers 7.65 and 9 mm (Walther) and a .357 caliber revolver (Smith & Wesson, 6 in. (15.24 cm) barrel) loaded with ammunition from a number of various manufacturers have been subjected to SPME sampling. The sampling was performed one day after shooting. Table 1 summarizes the results. Different amounts of TEA2 compound were deposited in firearm barrels on shooting with ammunition from different manufacturers. There was no clear correlation between the amount of TEA2 and caliber of ammunition used. In most experiments, however, more TEA2 was detected in 9 mm caliber pistols by comparison with that for 7.65 mm caliber from the same manufacturer. All the experiments with one exception resulted in the detection of the TEA2 peak inside pistol/revolver barrels one day after shooting. In shooting with CCI Blazer 9 mm ammunition (lead-free), the TEA2 peak was not observed. Large concentrations of nitroglycerine (NG) detected in this ammunition may be one explanation—NG and TEA2 compound may compete for the same adsorption sites on the SPME fiber.

For nonexponential decays of TEA2 compound detected inside shotgun (1) and rifle (4) barrels, a simple mathematical curve fitting procedure was proposed for the estimation of time since the latest discharge when the ammunition used is unknown. We feel that the use of this procedure for weak TEA2 peak detected in pistols and revolvers would be limited. Instead the observation of TEA2 compound inside small-arms barrels should be interpreted as showing that the firearm had been fired recently, maximally in the previous 1–2 weeks. This can only be applied to firearms stored at

approximately room temperature, not below 20°C. We do not examine firearms found outdoors, as the temperature of the storage and other weather conditions are not controllable.

The surface of the inside of pistols and revolvers is rifled. Thus, the number of shots may influence the results in a manner similar to that observed for rifles (4). We have carried out only a few experiments with pistols. After firing four shots with these firearms, the amount of TEA2 compound increased approximately 50% compared to that after firing a single shot. Cleaning the firearm afterwards with a cloth removed part of the decomposition products from the barrel. As in the case of rifles, a careful cleaning of small arms with oil seriously restricts the possibility of estimation of time since the latest discharge of the firearm.

Preventing the Escape of the TEA2 Compound from the Barrel

This study shows that the amount of TEA2 compound detected inside pistol and revolver barrels is very low and its escape from the barrel rapid. It would be a definitive advantage to prevent this compound from escaping the barrel and to keep its concentration at the same level as when the firearm was found until the investigation of the forensic laboratory could be started.

In our previous study with shotguns (1) we tried to seal shotgun barrels with corks. Unfortunately, this procedure had no detectable effect on the decay of the TEA2 peak. This decay is, however, strongly influenced by temperature of storage. These observations indicate that the decay studied is rather the decomposition than the escape of volatile TEA2 compound from the barrel. When a firearm is stored at very low temperatures, the decay of the TEA2 peak will be so slow that the process is practically stopped.

We have performed the following experiment. A 7.65 mm Walther pistol was used. First SPME sampling was carried out one day after shooting with Federal ammunition. After this sampling the pistol was placed in a freezer where the temperature was kept at −25°C and stored there for three weeks. Afterwards, the pistol was removed from the freezer and sampled once again when it reached room temperature. Figure 5 shows the results of these two samplings. The amount of TEA2 compound detected after the three
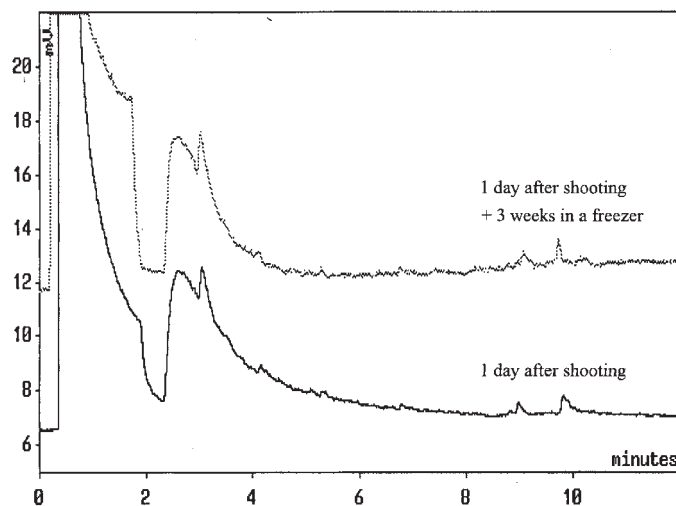

FIG. 5—*Amount of TEA2 compound detected inside a 7.65 mm Walther pistol. The first SPME sampling (connected line) was carried out at room temperature one day after shooting with Federal ammunition. The pistol was then put in the freezer for three weeks. The second sampling (dashed line) was done again at room temperature after this cooling period. The TEA2 peak height in these two samplings is practically the same.*

weeks of storage at $-25°C$ was within the experimental error of the method the same. Freezing the firearm seems to be a process suitable for storing pistols and revolvers in situations when the laboratory investigation cannot be started immediately.

Effect of Length of the Barrel

It is expected that the length of the firearm barrel influences the amount of decomposition products deposited on the inner walls of the barrel. Burning characteristics inside the barrel and the amount of soot particles formed will be different. We performed the following test to evaluate the effect of the barrel length on the amount of TEA2 compound detected. Three firearms with lengths of barrel ranging from 9 cm (including the chamber) to 61 cm were employed in this test. The firearms were loaded with the same ammunition—caliber .22 LR Super Speed, manufactured by Winchester. All ammunition was taken from the same ammunition box. The SPME sampling was carried out from the muzzle position one day after firing of a single shot with each of the weapons. Table 2 shows the results. The amount of TEA2 compound expressed as peak height of the TEA2 peak increased enormously with the increased length of the barrel. The amount found in the rifle (Mossberg & Sons) was comparable to that detected in shotguns loaded by shotgun ammunition where the quantity of the propellant used is much higher.

Example from Casework

One example from our recent casework might illustrate the use of the method described in the text. Four Sig Sauer pistols, caliber 9 mm were submitted to our laboratory for estimation of time since the latest discharge. It was suspected that all these firearms were fired recently and on the same day. Due to holidays and other delays, the laboratory investigation was started as late as four days after the police received the firearms. Such a delay may result in the TEA2 compound escaping from the barrel and thus will not be detected. Therefore, the SPME sampling at the laboratory was prolonged to 60 min. The TEA2 peak was detected in all four firearms and its decay could be measured for about one week. This decay was rapid and followed similar curves for all the weapons. In three of the weapons the height of the TEA2 peak was about the same, in one of the weapons this peak was 50% stronger. Figure 6 shows the decay observed for this particular weapon. No curve fitting procedure was carried out in this case and the conclusion was only that all the weapons investigated were fired very recently, just a short time before their seizure. According to the actual account we subsequently received, the pistols were fired one day before their seizure and consequently five days before the examination was started at the laboratory. The same kind of ammunition was used in all the firearms. Single shots were fired with three of the pistols, whereas the pistol with the highest amount of TEA2 compound was fired four times on that occasion.

TABLE 2—*Effect of barrel length on amount of combustion products detected. The ammunition used was Winchester 22 long rifle type, Super Speed, the same batch in each shooting. The SPME sampling was taken at the muzzle about 6 cm inside the bore.*

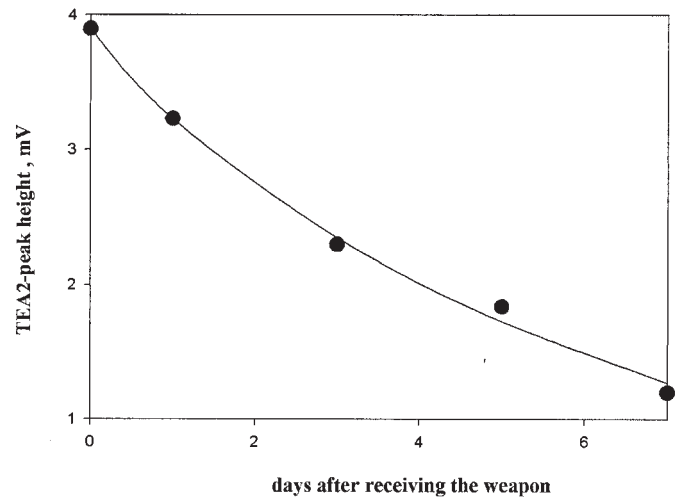| Type of Weapon (Caliber .22)	Length of Barrel (Incl. Cartridge Position)	TEA2 Peak Height
Pistol, Bernadelli	9 cm	2.4 mV
Pistol, Druvlov	24.5 cm	170 mV
Rifle, Mossberg & Sons	61 cm	3100 mV

FIG. 6—*Decay of the TEA2 peak with time from the barrel of a Sig Sauer pistol, caliber 9 mm, encountered recently in our casework. A prolonged, 60-min SPME sampling at room temperature was carried out. As we later were informed, the firearm had been used five days before the examination started at the laboratory.*

Conclusion

The GC/TEA system can be used for detection of the TEA2 compound inside pistol and revolver barrels. The amount of this compound is very low; therefore, a prolonged sampling time is recommended. In this study, a 40-min SPME sampling was employed, but the sampling time can be prolonged even more to improve the sensitivity of the detection.

The escape of TEA2 compound from pistol and revolver barrels with time is rapid and can generally be measured for only a few days after the latest discharge. The decay curve is nonexponential, but the curve-fitting procedure for estimation of time since the discharge would be inexact. Instead, the detection of TEA2 compound in small-arm barrels should be interpreted that the firearm has recently been fired.

When the suspect firearm is stored at $-25°C$, the decay of TEA2 compound is practically stopped. This procedure is suitable when the laboratory investigation for some reason cannot be started immediately.

For pistols and revolvers false negative observations might be encountered. The TEA2 peak is not necessarily detected in recently fired weapons, when ammunition containing large amounts of nitroglycerine is used.

References

1. Andrasko J, Norberg T, Ståhling S. Time since discharge of shotguns. J Forensic Sci 1998;43(5):1005–15.
2. Andersson C, Andrasko J. A novel application of time since the latest discharge of a shotgun in a suspect murder. J Forensic Sci 1999; 44(1):209–11.
3. Andrasko J, Ståhling S. Time since discharge of spent cartridges. J Forensic Sci 1999;44(3):487–95.
4. Andrasko J, Ståhling S. Time since discharge of rifles. J Forensic Sci 2000;45(6):1250–5.

Additional information and reprint requests:
Jan Andrasko, Ph.D.
SKL, National Laboratory of Forensic Science
SE—581 94 Linköping, Sweden